MULTIPLET SEPARATION FACTORS IN THE SPECTRUM OF CHROMIUM II

By V. SURYANARAYANA and V. RAMAKRISHNA RAO
DEPARTMENT OF PHYSICS, ANDHRA UNIVERSITY, WALTAIR

(*Received for publication, April 10, 1954*)

ABSTRACT. Formulae for the multiplet separation factors in the configurations $3d^4.4s$ and $3d^4.4p$ are derived and used for the calculation of the multiplet separations. The values are compared with the experimental data.

INTRODUCTION

In continuation of our earlier work on the term values of Cr II, the multiplet separation factors in the configurations $3d^4.4s$ and $3d^4.4p$ were calculated. The theory of multiplet separation factors was given for equivalent electron configuration by Goudsmit (1928) and for the addition of an s or p electron by Goudsmit and Humphreys (1928). The working details may again be found in two papers by V. R. Rao (1938). The formulae for $3d^4.4s$ and $3d^4.4p$ were not available in literature as far as we were aware and so were derived by us. The results are described below.

CONFIGURATION $3d^4$

Table I gives the results for $3d^4$ configuration. The theoretical values for A, the multiplet separation factor, is zero, in every term. The experimental values, as given in the last column, are all very nearly equal to zero for all sextet and quartet terms. In the term scheme we find a partial invertion of the multiplet levels as in a $a^4G_{2\frac{1}{2}}$ to $a^4G_{5\frac{1}{2}}$. This means that in the actual spectrum, the lines are very close together and occur in no definite order. For the assignments of such lines the method of constant differences is not of much help and evidence from Zeeman effect and hyperfine structure studies would be essential.

CONFIGURATIONS $3d^4.4s$ AND $3d^4.4p$

The formulae for the multiplet separations in these configurations were derived by us and given in column 3 in Tables II and III. They are obtained by considering the value of (A') in the configuration $3d^4$ of Cr III and given in terms of a. In the case of $3d^4.4p$ the individual formulae contain terms in a_2 also, which is the contribution by a p electron to the value in $3d^4$. These a_2 values are not capable of evaluation and so they have to be eliminated by taking $\Sigma A'$ for (1) all terms of same multiplicity or (2) all terms of same L value and so on.

TABLE I

Multiplet separations in the observed terms of Cr II $3d^5$ configuration

Term	$\Delta\nu$	Separation factor (A)
$a^6S_{2\frac{1}{2}}$	0.0	0.0
$a^4G_{2\frac{1}{2}}$ $G_{3\frac{1}{2}}$ $G_{4\frac{1}{2}}$ $G_{5\frac{1}{2}}$	5.7 1.5 −7.1	.08
$a^4P_{\frac{1}{2}}$ $P_{1\frac{1}{2}}$ $P_{2\frac{1}{2}}$	0.6 −1.9	−0.33
$b^4D_{\frac{1}{2}}$ $D_{1\frac{1}{2}}$ $D_{2\frac{1}{2}}$ $D_{3\frac{1}{2}}$	7.5 3.9 −13.1	−0.23
$a^2I_{5\frac{1}{2}}$ $I_{6\frac{1}{2}}$	6.4	+0.98
$a^2D_{2\frac{1}{2}}$ $D_{1\frac{1}{2}}$	−180.5	−72.2
$a^2F_{3\frac{1}{2}}$ $F_{2}1/2$	−247.8	−70.8
$b^4F_{1\frac{1}{2}}$ $F_{2\frac{1}{2}}$ $F_{3\frac{1}{2}}$ $F_{4\frac{1}{2}}$	19.7 −18.3 17.6	0.95
$b^2H_{4\frac{1}{2}}$ $H_{5\frac{1}{2}}$	97.2	17.7
$a^2G_{3\frac{1}{2}}$ $G_{4\frac{1}{2}}$	170.8	38.0
$c^2F_{2\frac{1}{2}}$ $F_{3\frac{1}{2}}$	134.9	38.5
$b^2S_{\frac{1}{2}}$	0.0	0.0
$d^2D_{2\frac{1}{2}}$ $D_{1\frac{1}{2}}$	−18.1	−7.2
$d^2G_{3\frac{1}{2}}$ $G_{4\frac{1}{2}}$	23.2	5.15

The observed data given in this table are due to Keiss (1951)

Table II contains the data on $3d^4.4s$ configuration. The experimental values of A are calculated both from adjacent levels and total separation and average values are given in column 7. These are to be compared with the calculated values given in column 8. We find in $3d^4.4s$ configuration there is a good agreement. The inverted nature of c^4D and b^2D was also observed experimentally.

In the configuration $3d^4.4p$, the value of A' (Cr III) is calculated from that of A (Cr II) by the formulae and given in column (7) in Table III.

TABLE II

Multiplet separation factor calculation in the terms of Cr II $3d^4.4s$ configuration.

Configuration and base term	Term	(1) Formula for A in terms of A'	(2) Separation factor (A) in terms of (a)	Separation factor (A) calculated from: adjacent levels	Total separation	Average value	(A) calculated from formula (2)
... ...	$*a^6D$	$A=4A'/5$	$A= a/5$	47 1,46 1 44.6,42 8	44 6	41 6	43 9
$3d^4(a^5D)4s$	$*a^4D$	$A=6A'/5$	$A=3a/10$	68.6,66 7 64.6	66.1	66.5	65 9
$3d^4(a^3P_-)4s$	b^4P_-	$A=2A'/3$	$A= a/3$	237,222.8	228 1	229 3	73 2
$3d^4(\ ^3P_+)4s$	$^4P_+$	$A=2A'/3$					
$3a^4(a^3P_-)4s$	a^4F_-	$A=2A'/3$	$A= a/18$	13 8,14 7 11.3	13 0	13 2	12.2
$3d^4(\ ^3F_+)4s$	$^4F_+$	$A=2A'/3$					
$3d^4(a^3P_-)4s$	a^2P_-	$A=4A'/3$	$A=2a/3$	464 4	464.4	464.4	146.5
$3d^4(\ ^3P_+)4s$	$^2P_+$	$A=4A'/3$					
$3d^4(a^3F_-)4s$	b^2F_-	$A=4A'/3$	$A= a/9$	11.0	11 0	11.0	24 4
$3d^4(\ ^3F_+)4s$	$^2F_+$	$A=4A'/3$					
	c^4D	$A=2A'/3$	$A=-a/18$	−22.5.−19.1	−16 9	−17 9	−12.2
$3d^4(a^3,D4s$	b^2D	$A=4A'/3$	$A=-a/9$	−13.0	−35.4	−35.4	−24 4
$3d^4(a^3G)4s$	b^4G	$A=2A'/3$	$A= a/10$	−35 4 29 5.21.9	20 4	21.4	22.0
$3d^4(a^3G)4s$	c^2G	$A=4A'/3$	$A= a/5$	13.7 31 2	31.2	31.2	43.9
$3d^4(a^3H)4s$	$*a^4H$	$A=2A'/3$	$A= a/15$	13.8,14 5 14.3	14.3	14.2	14.7
$3d^4(a^3H)4s$	a^2H	$A=4A'/3$	$A=2a/15$	33.1	33.1	33.1	29.3
$3d^4(a^1S)4s$	a^2S	$A=0$	$A=0$	0.0	0.0	0.0	0.0
$3d^4(a^1G)4s$	b^2G	$A=0$	$A=0$	12.0	12.0	12.0	0.0
$3d^4(a^1D)4s$	c^2D	$A=0$	$A=0$	24 5	24.5	24.5	0 0
$3d^4(\ ^1S)4s$	^2S	$A=0$	$A=0$				0.0
$3d^4(\ ^1D)4s$	^2D	$A=0$	$A=0$				0.0
$3d^4(a^1F)4s$	d^2F	$A=0$	$A=0$	−5.9	−5.8	−5.8	0 0
$3d^4(\ ^1G)4s$	^2G	$A=0$	$A=0$	—	—	—	0.0
$3d^4(a^1I)4s$	b^2I	$A=0$	$A=0$	−4.1	−4.1	−4.1	0.0

$a=219.7$

The base terms with no suffix before them are only theoretically possible terms and are not experimentally identified.

The values of the terms with asterisks are employed in the calculation of the value of a.

The mean value of A' obtained from various sources (like all 'P' terms, or all sextets etc. arising out of the same base term) is given at the end of the same column. This is to be compared with the value given in the last

TABLE III

Electron configuration	Term	Equation	Separation factor A calculated from: Adjacent levels	Separation factor A calculated from: Total separation	Separation factor A calculated from: Mean value	A' calculated from (A)	Separation factor A' calculated from the ion data: Adjacent levels	Separation factor A' calculated from the ion data: Total separation	Separation factor A' calculated from the ion data: Mean value
$3d^4(a^5D)4p$	z^6P	$A=6A'/5-a_2/10$	36.9, 40.3	36.9	38.7				
$l'=2$, $s'=2$									
$l_2=1$, $s_2=1/2$	z^6D	$A=2A'/3+a_2/30$		28.7	28.7				
	z^6F	$A=8A'/15+a_2/15$	54.6, 54.0, 55.4, 52.8, 52.2	51.6	53.1				
	z^4P	$A=9A'/5+a_2/10$	171.1, 138.3	150.6	153.3				
	z^4D	$A=A'-a_2/30$	54.4, 50.4, 45.4	48.9	49.8				
	z^4F	$A=4A'/5-a_2/15$	34.1, 34.1, 34.1	34.1	34.1		60.0, 60.0, 57.3, 55.0,	57.2	57.9
	P terms	$\Sigma A=3A'$				64.0			
	D terms	$\Sigma A=5A'/3$				47.1			
	F terms	$\Sigma A=4A'/3$				65.5			
	All sextets	$\Sigma A=12A'/5$				59.2			
	All quartets	$\Sigma A=18A'/5$				65.9			
		Total $\Sigma A=6A'$				59.6			

Mean value of A'. 58.6

TABLE III (contd.)

Electron configuration	Term	Equation	Separation factor A calculated from			A' calculated from (A)	Separation factor A' calculated from the ion data		
			Adjacent levels	Total separation	Mean value		Adjacent levels	Total separation	Mean value
$3d^4(a^3H)4p$	z^4G	$A = 12A'/15 - a_2/15$	28.5, 29 2, 59.2	40.9	39.5				
$l'=5,\ s'=1$	z^4H	$A = 58A'/90 + a_2/90$	23.4, 25.9, 28.0	26 0	25.8				
$l_2=1,\ s_2=1/2$	z^4I	$A = 5A'/9 + a_2/18$	36.8, 30.5, 25 9	30.5	30.9				
	z^2G	$A = 8A'/5 + a_2/15$	30 5	30.5	30.5				
	z^2H	$A = 58A'/45 - a_2/90$	47 4	47 4	47 4				
	z^2I	$A = 10A'/9 - a_2/18$	12.7	12.7	12.7				
	G terms	$\Sigma A = 12A'/5$				29 2	24.8, 22.7	23 6	23 7
	H terms	$\Sigma A = 29A'/15$				37.9			
	I terms	$\Sigma A = 5A'/3$				26.2			
	All quartets	$\Sigma A = 2A'$				48 2			
	All doublets	$\Sigma A = 4A'$				22.6			
		Total $\Sigma A = 6A'$				25 6			

Mean value of A' 31.6

TABLE III (contd.)

Electron configuration	Term	Equation	Separation factor A calculated from: Adjacent levels	Separation factor A calculated from: Total separation	Separation factor A calculated from: Mean levels	A' calculated from A	Separation factor A' calculated from the ion data: Adjacent levels	Separation factor A' calculated from the ion data: Total separation	Separation factor A' calculated from the ion data: Mean value
$3^4d(a^3G)4P$	x^4F	$A=5A'/6-a_2/12$		14.3	14.3				
$l'=4,\ s'=1$	x^4G	$A=19A'/30+a_2/60$	31.5, 56.0, 36.5	41.7	41.4				
$s_1=1,\ s_2=1/2$	y^4H	$A=8A'/15+a_2/15$	32.0, 32.4, 33.5	33.0	33.0				
	Y^2F	$A=5A'/3+a_2/12$		76.5	76.5				
	x^2G	$A=10A'/15-a_2/60$		15.1	15.1				
	y^2H	$A=16A'/15-a_2/15$		0.83	0.83				
							37.5, 28.4	32.4	32.4
	F terms	$\Sigma A = 5A'/2$				36.3			
	G terms	$\Sigma A = 19A'/10$				29.8			
	H terms	$\Sigma A = 8A'/5$				21.1			
	All quartets	$\Sigma A = 2A'$				44.3			
	All doublets	$\Sigma A = 4A'$				23.1			
		Total $\Sigma A = 6A'$				30.2			

Mean value of A'.. 30.8

TABLE III (contd.)

Electron configuration	Term	Equation	Separation factor A calculated from			A' calculated from (A)	Separation factor A' calculated from the ion data		
			Adjacent levels	Total separation	Mean value		Adjacent levels	Total separation	Mean value
$3d^4(a^3F)4p$ $l'=3$, $s'=1$	x^4D	$A=8A'/9-a_2/9$		1.1	1.1				
$l_2=1$, $s_2=1/2$	y^4F	$A=11A'/18+a_2/36$	3.0, 1.9, 12.2	3.3	5.1				
	y^4G	$A=A'/2+a_2/12$		1.8	1.8				
	y^2D	$A=16A'/9+a_2/9$		126.2	126.2				
	z^2F	$A=11A'/9-a_2/36$		50.4	30.4				
	y^2G	$A=A'-a_2/12$		45.4	45.4				
	D terms	$\Sigma A=8A'/3$				47.7			
	F terms	$\Sigma A=11A'/6$				30.3			
	G terms	$\Sigma A=3A'/2$				31.2			
	All quartets	$\Sigma A=36A'/18$				4.0			
	All doublets	$\Sigma A=4A'$				55.2			
		Total $\Sigma A=6A'$				38.1			
$3d^4(b^3F)4p$	u^2G	$A=A'-a_2/12$		26.0	26.0				
$l'=3$ $s'=1$						*− 5.6			
$l_2=1$ $s_2=1/2$	u^2D	$A=16A'/9+a_2/9$		−25.1	−25.1				

Mean value of A' ... 34.4

TABLE III (contd.)

Electron configuration	Term	Equation	Separation factor A calculated from			A' calculated from (A)	Separation factor A' calculated from the ion data		
			Adjacent levels	Total separation	Mean value		Adjacent levels	Total separation	Mean value
$3d^4(a^3D)4p$	x^4P	$A = A'-a_2/6$	−93.5, 135.2	−109.1	−112.6				
$l'=2,\ s'=1$	w^4D	$A = 5A'/9+a_2/18$	3.5, 9.7, 14.1	10.5	9.5				
$l_2=1,\ s_2=1/2$	w^4F	$A = 4A'/9+a_2/9$	18.2, 30.0, 18.0	22.0	22.0				
	y^2P	$A = 2A'/+a_2/6$	87.2	87.2	87.2				
	x^2D	$A = 10A'/9-a_2/18$	−69.8	−69.8	−69.8				
	x^2F	$A = 8A'/9-a_2/9$	91.9	91.9	91.9				<u>−19</u>
	P terms	$\Sigma A = 3A'$				8.4			
	D terms	$\Sigma A = 5A'/3$				36.2			
	F terms	$\Sigma A = 4A'/3$				85.4			
	All quartets	$\Sigma A = 2A'$				40.6			
	All doublets	$\Sigma A = 4A'$				27.3			
		Total $\Sigma A = 6A'$				4.7			

Mean value of A' ... 33.8

The underlined value of A' given in the last column of the table is not experimentally observed but is calculated from the observed data for Cr III itself.

TABLE III (contd.)

Electron configuration	Term	Equation	Separation factor A calculated from: Adjacent levels	Separation factor A calculated from: Total separation	Separation factor A calculated from: Mean value	A' calculated from (A)	Separation factor A' calculated from the ion data: Adjacent levels	Separation factor A' calculated from the ion data: Total separation	Separation factor A' calculated from the ion data: Mean value
$3d^4(a^3P)4p$ $l'=1,\ s'=1$	y^4D	$A=A'/3+a_2/6$	172.9, 154.8, 135.8	149 6	153.3				
$l_2=1,\ s_2=1/2$	y^4P	$A=A'/3+a_2/6$	65.9, 148 8	117.6	110.8				
	z^4S	$A=0$	0.66	0.66	0.66				
	z^2D	$A=2A'/3-a_2/6$	145 0	145 9	145.0				
	z^2P	$A=2A'/3-a_2/6$	132.2	132.2	132.2				
	z^2S	$A=0$	0	0	0				
	D terms	$\Sigma A=A'$				298.3	342.0	342.0	342 0
	P terms	$\Sigma A=A'$				243.0			
	S terms	$\Sigma A=0$							
	All puartets	$\Sigma A=2/3A'+a_2/3$							
	All doublets	$\Sigma A=4A'/3-a_2/3$							
		Total $\Sigma A=2A'$							

Mean valne of A' ... 270.5

TABLE III (contd.)

Electron configuration	Term	Equation	Separation factor A calculated from			A' calculated from (A)	Separation factor A' calculated from the ion data		
			Adjacent levels	Total separation	Mean value		Adjacent levels	Total separation	Mean value
$3d^4(a^1I)4p$	z^2K	$A=a_2/7$	28.7	28.7	28.7				
	y^2I	$A=a_2/42$	0.4	0.4	0.4				
	x^2H	$A=-a_2/6$	45.7	45.7	45.7				
		total $\Sigma A=0$							
$3d^4(a^1F)4p$	v^2D	$A=-a_2/3$	−1.5	−1.5	−1.5				
	u^2F	$A=a_2/12$	20.7	20.7	20.7				
	v^2G	$A=a_2/4$	81.4	81.4	81.4				
		total $\Sigma A=0$							
$3d^4(a^1D)4p$	w^2P	$A=-a_2/2$	44.0	44.0	44.0				
	w^2D	$A=a_2/6$	52.9	52.9	52.9				
	v^2F	$A=a_2/3$	57.0	57.0	57.0				
		total $\Sigma A=0$							

TABLE III (contd)

Electron configuration	Term	Equation	Separation factor A calculated from			A' calculated from (A)	Separation factor A' calculated from the ion data		
			Adjacent levels	Total separation	Mean value		Adjacent levels	Total separation	Mean value.
$3d^4(a^1G)4p$	w^3F	$A = -a_2/4$	-31.1	-31.1	-31.1				
	w^3G	$A = a_2/20$	20.8	20.8	20.8				
	w^3H	$A = 12a_2/60$	-34.8	-34.8	-34.8				
		total $\Sigma A = 0$							
$3d^4(a^1S)4p$	^1S	$A = a_2/0$							
	x^3P	$A = a_2$	-42.6	-42.6	-42.6				
		Total $\Sigma A =$							

The values of (A') marked with asterisk for the term b^3F in $3d^4.4p$ configuration are obtained by solving the two equations for the terms u^3G and u^3D.

column for A' as calculated from the ion data (Cr III). The agreement is quite good in the case of ^5D, ^3H and ^3G. In the case of ^3P and ^3F terms both of which occur twice in the configuration $3d^4$, the agreement is not satisfactory. In case of such teams only an average value of the separation factor for the two similar terms is given by the formula. In general both the terms are rarely observed and unless we have the data of both the terms, it is not possible to take the average value from the experimental data. In case of ^3D the value given in column 10 is obtained by calculation from Cr III data itself. It was not observed experimentally. This might possibly account for the considerable discrepancy between this value and the one shown in column 7. The case of doublets of Cr II arising out of singlets of Cr III is interesting. The A' factors are zero. So the A factor is obtained in terms of a_2. The values of A for all terms arising out of the same base term are zeroes as can be seen from Table III. From the nature of the formula it appears as if we can calculate the value of a_2 from the experimental value of the separation factor A for a few doublets. However, on comparison with a few such calculated values, the values of a_2 is found to be very erratic. Evidently no useful information could be obtained from these data. The separation factor for the added p electron a_2 is not capable of direct calculation.

ACKNOWLEDGMENT

The authors wish to take this opportunity to express their thanks to Prof. K. R. Rao for his kind interest in the work.

REFERENCES

Bowen, 1937, *Phys. Rev.*, **52**, 1153.
Goudsmit, 1928 *Phys. Rev.*, **31**, 946.
Goudsmith and Humphreys, 1928, *Phys. Rev*, **31**, 960.
C. C. Kiess, 1951, *J. Res. Nat. Bur. Stand.*, **47**, 423.
V. R. Rao and K. R Rao, 1948, *Ind. J Phys.*, **22**, 175
V. R. Rao and K. R. Rao 1948, *Ind. J Phys.*. **22**, 180